

# Hybrid Exciton State in Quantum Dot- Dendrite System: The Green Functions

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## Abstract

A model is proposed to study the hybrid exciton in a quantum dot-dendrimer systems. The semiconductor organic hybrid exciton is studied using a "real space" Green's function method and a diagrammatic technique. The energy of the hybrid exciton as well as the Green function matrix elements have been calculated for different quantum dot-dendrimer systems, and the method can be applied for systems with different structures. Using the double-time Green's functions the optical processes can be calculated. The optical properties of the systems are controllable by the size and structure of the QD-dendrimer systems.

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## I.Introduction.

With the development of nano- and biotechnology, at present dendrimers and dendrimeric systems are being studied intensively and many systems have become available[1-6]. Dendrimers are nanosize, highly symmetric and perfectly hyperbranched macromolecules with controlled structure, which are good candidates to behave as optimal energy funnels. Dendrimers with controllable sizes and structure can be used as light emitters and can serve as building blocks in nano-devices [3].

Recent studies support the interest in preparing systems with the combination of properties of semiconductor nanocrystal and organic dendrimer. Semiconductor nanocrystals, or quantum dots, which are semiconductor spheres with radius around  $30\text{\AA} - 100\text{\AA}$ , have very strong quantum confinement effects. These quantum size effects of the motion and behavior of the carriers like electrons and holes lead to many interesting optical and structural phenomena[7-8]. The optical properties and optical processes of a quantum dot strongly depend on the dot size and therefore can be controlled by the size of the nanocrystals. The fact that the electronic states in the quantum dot are widely separated due to quantum confinement, and the emission region is controllable by changing the dot size makes it interesting to use the dot as a photoactive element at the center of the dendrimer. The emission can be tuned by changing the dot size as well as the structure of the dendrimer[4].

In a solid, excitons play a fundamental role in optical properties, for example by determining the optical processes happening close to the band gap. There are two kinds of excitons in solids. The Wannier Mott- exciton in semiconductors is relatively weakly bound with the Bohr exciton radius  $a_B \sim 30\text{\AA} - 100\text{\AA}$  and therefore is called the large-radius exciton. The Frenkel exciton is the electronic state of a molecular or strongly ionic crystal, strongly localized with the exciton radius  $a \sim 5\text{\AA}$ . But while the oscillator strength of the Wannier-Mott exciton is weak, the oscillator strength of the Frenkel exciton is very strong. Because of the difference between these two kind of exciton it would be interesting to create some system with an hybrid excitation state which has the composite properties of both kinds of exciton. Then one can expect to have an hybrid exciton with very strong oscillator strength as well as very large exciton radius. Several specific systems of this semiconductor-organic combination were proposed[9-12] such as a neighboring structure of organic and semiconductor quantum wells[9], neighboring organic and inorganic quantum wires[10], a single quantum dot in an organic shell[11] and the system of quantum dot array embedded in an organic host[12]. The obtained hybrid exciton also has been claimed to have very large non-linearities.

In this paper, we consider the hybrid exciton formed in the system with a quantum dot at the core of a dendrimer. In the quantum dot-dendrimer system, the Wannier exciton in the dot will interact with the Frenkel exciton in the dendrimer through dipole-dipole interaction to form some hybrid excitation. This hybrid exciton will play an important role in optical properties of the system and by changing the size and structure of the nanocrystal-dendrimer, one can expect to change the hybrid exciton properties and therefore to control optical processes of the system such as by tuning emission region or to change the nonlinear susceptibilities of the system.

We will use the Green's function approach to solve the problem. The double-time Green's functions in the real space with the diagram technique is very useful and important in solving

the problems with complicated structures. The Green's functions are directly related to properties of the system, so once the Green's functions are calculated, the optical properties such as non-linearities, fluorescence, scattering etc. can be evaluated.

## II. The Model for the Quantum Dot-Dendrite system

We consider a model of a quantum dot as a spherical core at the center, which is attached to three dendrimeric branches. Each dendrimeric branch consists of tertiary amine groups linked by three-carbon chains. Then each monomer unit (branching point) is attached to two protein branches, and so on (Fig.1). There is coupling between the quantum dot and the attached protein branches, between molecules in the same branches, as well as between the molecule at the branching point and the protein chain attached to it. But no coupling between molecules of different branches is assumed.

The Wannier exciton in the quantum dot and the Frenkel exciton in each organic molecule interact with each other through dipole-dipole interaction. Here we assume only nearest neighbor interaction.

The tight-binding Hamiltonian of the system can be written as the following:

$$H = \sum_{i=1}^N \mathcal{E}_i a_i^+ a_i + \sum_{i,j} V_{ij} a_i^+ a_j \quad (1)$$

Here  $a_i^+$ ,  $a_i$  are exciton creation and annihilation operators,  $\mathcal{E}_i$  is the exciton energy at each site, with  $i$  labelling the sites of quantum dot and molecules at the end of each generation of the dendrimeric branch. For the quantum dot the energy will be the energy of the exciton confined in the dot[8] and for the molecular sites it will be the Frenkel exciton energy.  $V_{ij}$  is the interaction integral between excitons in different sites, or in other words, between exciton of different dendrimer generations. Note that by  $i$  and  $j$  here we number sites in a "macroscopic" scale. Actually, at this scale  $i, j$  are the sites of the molecules at the branching point, i.e. the end of each generation. For example, the quantum dot is located at  $i = 0$ , the molecules of the monomer unit at the end of the first generation located at the site  $i = 1$ , etc... The molecules within each chain linking different generations are counted in the "microscopic scale". The interaction between molecules in the same chain causes the effective interaction between dendrimer generations. Namely, the interaction between molecules in the chain linking the site  $i$  with the site  $i+1$  makes up the interaction coefficient  $V_{ij}$ . So,  $V_{ij}$  actually is the effective interaction, that will be calculated in the section III.

We apply here the "real space" Green's function method developed in [13, 14]. The double-time Green's functions are written as

$$g_{ij} = \langle\langle a_i(t), a_j^+(0) \rangle\rangle = -i\Theta(t) \langle [a_i(t), a_j^+(0)] \rangle \quad (2)$$

where  $[,]$  is a commutator,  $a(t)$  is the Heisenberg representation of the operator  $a$ ,

$$a(t) = e^{iHt} a e^{-iHt} \quad (3)$$

$\Theta(t)$  is Heaviside function,  $\langle \dots \rangle$  is the thermal average over a grand canonical ensemble. Using the Fourier transformation to transfer the time Green's function to the energy variable, we have

$$g_{ij}(t) = \int_{-\infty}^{\infty} g_{ij}(E) e^{-iEt/\hbar} dE \quad (4)$$

By using the Green function

$$G_{ij}(E) = \frac{2\pi}{\hbar} g_{ij}(E) \quad (5)$$

and the Heisenberg equation of motion

$$i\hbar\dot{a}_j = \mathcal{E}_j a_j + \sum_i V_{ji} a_i \quad (6)$$

we have Schwinger-Dyson equations for the Green's functions for our system

$$(E - \mathcal{E}_i) G_{ij}(E) - \sum_{i,k} V_{ik} G_{kj}(E) = \delta_{ij} \quad (7)$$

Since the system consists of both Wannier and Frenkel excitons, the Green functions we consider here are the Green's function of hybridized state and  $E$  is the energy of the new excitation.

In the next section we will calculate the effective interaction coefficients  $V_{ij}$ , then in the following sections we will apply the Schwinger equations (7) to solve for our system.

### III. The effective interaction coefficients

As it has been said in the section II, the interaction between different generations, called the interaction at a macroscopic scale, has been made from all the interactions between nearest neighboring molecules, called the interaction at the microscopic scale. For example, we consider a chain as in the Fig.2a. We want to calculate the interaction between the quantum dot at the center, which we can consider as the zero-generation, and the molecule at the end of one of the first molecular chains, which is the first generation. In the chain there is a number of molecules, so the quantum dot and the molecule finishing the first generation may be far apart and do not interact directly with each other if we assume only nearest neighbor interaction. So the exciton in the quantum dot interacts with the exciton in the first molecule of the first chain, the first molecule interacts with the second molecule, and so on, the next to the last molecule interacts with the last molecule of the chain. Actually in this process the exciton in the quantum dot interacts with the exciton in the last molecule of the first chain indirectly through the effective "superexchange" interaction. The problem is very similar to the problem of electron transfer in a chain with one impurity [15]. In this section we use the Green's function and renormalization approach [15, 16] to calculate the effective interaction.

As in [15], for the linear chain we consider the Huckel Hamiltonian:

$$H = \sum_i \epsilon_\alpha a_\alpha^\dagger a_\alpha + \sum_{\alpha,\beta} v_{\alpha,\beta} (a_\alpha^\dagger a_\beta + a_{\beta,a_\alpha}^\dagger) \quad (8)$$

$a_\alpha^\dagger, (a_\alpha)$  are the creation (annihilation) exciton operator at the site  $\alpha$ .  $v_{\alpha,\beta}$  is the interaction of excitons at site  $\alpha$  and site  $\beta$ . Here we assume only nearest neighbor interaction, so

$\beta = \alpha \pm 1$ .  $\alpha$  numbers sites of the linear chain, namely if our linear chain consists of  $n$  molecules, the quantum dot lies at the site  $\alpha = 0$ , and the molecules lie at sites  $1, 2, \dots, n$ . The nearest neighbor interaction between excitons in adjacent sites is  $v_{\alpha, \alpha+1}$ , where  $v_{01}$  is the interaction between the Wannier exciton in the quantum dot and the Frenkel exciton in the organic molecule, and all other  $v_{12}, v_{23}, \dots, v_{n-1, n}$  are the interaction between the Frenkel excitons in the molecules. Then  $v_{0n}$  will be the effective interaction between the quantum dot and the first generation in the "macroscopic scale". Then we can replace the chain by the quantum dot and the last molecule of the chain interacting with each other through  $v_{0n}$ . The Dyson's equation for this Hamiltonian [15]:

$$Eg_{\alpha\beta} = \sum_k H_{\alpha k} g_{k\beta} \quad (9)$$

For our chain (Fig.2a) this equation can be written as:

$$\begin{aligned} (E - \epsilon_0)g_{00} &= 1 + v_{01}g_{10} \\ (E - \epsilon_1)g_{10} &= v_{10}g_{00} + v_{12}g_{20} \\ (E - \epsilon_2)g_{20} &= v_{21}g_{10} + v_{23}g_{30} \\ &\dots \\ (E - \epsilon_{n-1})g_{n-1,0} &= v_{n-1,n-2}g_{n-2,0} + v_{n-1,n}g_{n0} \\ (E - \epsilon_n)g_{n,0} &= v_{n,n-1}g_{n-1,0} \end{aligned} \quad (10)$$

Here  $\epsilon_0 = \epsilon_W$  is the energy of the Wannier exciton in the quantum dot,  $\epsilon_1, \epsilon_2, \dots, \epsilon_n$  are the energies of the Frenkel excitons in the molecules. since we consider the dendrimetic chain of identical molecules, so we can assume all  $\epsilon_1, \epsilon_2, \dots, \epsilon_n = \epsilon_F$ . Also, except for the dot-molecule Wannier exciton-Frenkel exciton interaction  $v_{01} = v_{WF}$ , all other  $v_{i,i+1} = v$  are the same. Then the system (10) becomes:

$$\begin{aligned} (E - \epsilon_W)g_{00} &= 1 + v_0g_{10} \\ (E - \epsilon_F)g_{10} &= v_0g_{00} + vg_{20} \\ (E - \epsilon_F)g_{20} &= vg_{10} + vg_{30} \\ &\dots \\ (E - \epsilon_F)g_{n-1,0} &= vg_{n-2,0} + vg_{n0} \\ (E - \epsilon_n)g_{n,0} &= vg_{n-1,0} \end{aligned} \quad (11)$$

Outside the defect region ( $i > 2$ ), the Green's functions of neighboring sites are supposed to be related to each other by some transfer function  $T$  with  $G_{i+1,0} = TG_{i,0}$ . By replacing this relation into the third and the following equations in the system (10), we obtain for the transfer function  $T$ :

$$T = \frac{E - \epsilon_F \pm \sqrt{(E - \epsilon_F)^2 - 4v^2}}{2v} \quad (12)$$

and for the Green's functions

$$\begin{aligned}
g_{00} &= \frac{1}{E - \epsilon_W - \frac{v_0^2}{E - \epsilon_F - vT}} \\
g_{10} &= \frac{v_0}{E - \epsilon_F - vT} g_{00}
\end{aligned} \tag{13}$$

and

$$g_{n0} = \frac{v_0}{E - vT} T^{n-1} g_{00} \tag{14}$$

from here we can have the "effective" interaction between site 0 and site n, or between the exciton in the quantum dot and the Frenkel exciton of the first dendrimeric generation:

$$v_{0n} = \frac{v_0}{E - vT} T^{n-1} = V_{WF} \tag{15}$$

And from the Green's function (13) we can have for the energy E of the mixed state in this chain

$$E = \epsilon_W + \frac{v_0^2}{E - \epsilon_F - vT} \tag{16}$$

In this fashion we already obtain the "effective" interaction between exciton in the quantum dot and the exciton of the first generation. Similarly we have the effective interaction between the Frenkel excitons in the neighboring generations like between the first and the second generations or between the second and the third etc...Like  $V_{WF}$ , this effective interaction  $V_{FF}$  is also made up of all the nearest neighbor interactions between the excitons of the molecules in the chain connected the last molecules of the two generations (Fig.2b). Similar to (15) we have

$$V_{FF} = \frac{v}{E - vT} T^{n-1} \tag{17}$$

and the energy in the chain

$$E = \epsilon_F + \frac{v^2}{E - \epsilon_F - vT} \tag{18}$$

Again, n is the number of molecules in the chain.

We note here that the "effective interaction" depends on the energies of excitons, the nearest neighbor interaction coefficients, and also on the number of molecules in the chain.

Now that we have all the needed interaction coefficients for the Schwinger-Dyson equation (7), we can replace the molecular chains by localized sites with effective interaction and we will apply this equation for our particular quantum dot-dendrimer system.

#### IV. Diagram Techniques for Green's Function in Orbital Representation

To solve the Schwinger-Dyson equations for the dendrimer system with many generations, it is convenient to use the "electron transfer graph" method developed in [13,14], where the method is used to study electron transfer between localized sites. Then for the Schwinger-Dyson equation (7), every site corresponds to a graph vertex. A non-diagonal term  $V_{jk}$  of

the Hamiltonian corresponds to an oriented edge originating at vertex  $j$  and ending at vertex  $k$  with the value of the edge equal to the interaction integral  $V_{jk}$ . Diagonal terms  $E - \mathcal{E}_{ii}$  of the Hamiltonian corresponds to a loop attached to the vertex  $i$  and the value of the loop equals  $W_{ii} = (E - \mathcal{E}_i)$ .

The details of the method and the proof of some formulae can be found in [13]. In this section we just write briefly about definitions and terminology, the main method and results of the authors[13] which we will use in the following sections.

In this diagram technique a path is a sequence of graph edges with successive edges originating at the point where the previous one ends, and a cycle is a path with the last edge ending at the point where the first one originates. A length of the path is the number of edges in it, where  $P_{ii} = 1$ . The value  $O$  of the cycle is the product of the values of all edges in the cycle, with the sign being negative except for the loop for any cycle with length more than 1. The cyclic term is a set of cycles which have no common vertice and pass through every vertex. The value of cyclic term  $\mathbf{O}$  is a product of the value of all cycles of the cyclic term and the cyclic value of the graph  $\Theta$  is the sum of all the cyclic terms.

For illustration, if the chain of sites is three sites as in Fig.3b, the cyclic term and the cyclic value of the graph will be as in the Fig.3c, or [13]:

$$\begin{aligned}\Theta_{1,3} &= \mathbf{O}_1 + \mathbf{O}_2 + \mathbf{O}_3 \\ &= (E - \mathcal{E}_1)(E - \mathcal{E}_2)(E - \mathcal{E}_3) - V_{12}V_{21}(E - \mathcal{E}_3) - V_{23}V_{32}(E - \mathcal{E}_1)\end{aligned}\quad (19)$$

For a chain of sites as in Fig.3a it is shown in [13] that the Green's function  $G_{ij}$  is equal to

$$G_{ij} = \frac{\Theta_{1,i-1}P_{ij}\Theta_{j+1,n}}{\sum O\{k\}} \quad (20)$$

where  $P_{ij}$  is the product of the edges along the pathway from vertex  $i$  to vertex  $j$

$$P_{ij} = V_{i,i+1}V_{i+1,i+2}\dots V_{j-1,j} \quad (21)$$

$\Theta = \sum O\{k\}(i, j)$  is the cyclic value of the graph and  $O_{ij}^{\{k\}}$  is the cyclic term.

Explicitly the Green functions have the form:

$$\begin{aligned}G_{11} &= \frac{1}{\Theta}[(E - \mathcal{E}_2)(E - \mathcal{E}_3) - V_{12}V_{21}] \\ G_{12} &= \frac{1}{\Theta}V_{12}(E - \mathcal{E}_3) = G_{21} \\ G_{13} &= \frac{1}{\Theta}V_{12}V_{23} = G_{31} \\ G_{22} &= \frac{1}{\Theta}(E - \mathcal{E}_1)(E - \mathcal{E}_3) \\ G_{23} &= \frac{1}{\Theta}(E - \mathcal{E}_1)V_{23} = G_{32} \\ G_{33} &= \frac{1}{\Theta}[(E - \mathcal{E}_1)(E - \mathcal{E}_2) - V_{23}V_{32}]\end{aligned}\quad (22)$$

For the case when there are sites of the sidegroup attached to some site  $i$  of the path (Fig.4a) then all the graph of the main chain remains the same, only the value of the loop at site  $i$  is

different. In this case it was proved in [13] that the diagonal element of the Green's function of side-graph can be expressed through the Green's function of subgraph in the continued fraction representation.

The value of the loop with the sidegroup could be expanded into continuous fraction of loops values of extended side graph  $\tilde{\gamma}$ -the subgraph of the graph. In another word, instead of the original loop value  $G_i^{-1} = W_{ii} = E - \mathcal{E}_i$  the loop value of the site with sidegroup becomes:

$$\begin{aligned}\tilde{G}_i^{-1} &= \tilde{W}_{ii} = (E - \mathcal{E}_i) - \sum_k \frac{V_{i,k}^2}{\tilde{\Theta}_{k(i)}/\Theta_{k(i)}} \\ &= (E - \mathcal{E}_i) - \sum_k V_{i,k(i)}^2 G(\tilde{\gamma}_k(i))_{kk}\end{aligned}\quad (23)$$

For illustration for the site chain in the Fig.4b the value of the loop at site 2 has the form:

$$\tilde{W}_{22} = E - \mathcal{E}_2 - \frac{V_{2a}V_{a2}}{E - \mathcal{E}_a - \frac{V_{ab}V_{ba}}{E - \mathcal{E}_b}} \quad (24)$$

by this continuous fraction representation we can count all the tree structure attached to any site of the chain.

Now we come back to consider our model of quantum dot-dendrimer system in the section II and apply this method to calculate the Green's function matrix elements for the hybridization excitation.

## V. The quantum dot- dendrimeric "slice"

As the first model for quantum dot-dendrimeric system, we consider the model in Fig.5a where a quantum dot is attached to a chain of molecules. The last molecule of this chain in its turn is connected to two chains, the last molecules of each is again connected with two other chain and so on. The number of branching points along one chain from the center to the terminal point is the generation number of the dendrimer. This model is very similar to the dendritic slice attached to the dot in several experiments[4,5].

Using the diagram with continous fraction representation we can consider the slice as a linear chain with sidegroups attached to each site. Then within this approximation where we neglect some symmetry in this structure the Fig.5a can be considered as the Fig. 5b.

For the quantum dot-dendrimer slice of 2 generations (Fig.5c) we have:

$$\Theta = (E - \mathcal{E}_W)(E - \mathcal{E}_F - \frac{V_{FF}^2}{E - \mathcal{E}_F})(E - \mathcal{E}_F) - V_{WF}^2(E - \mathcal{E}_F) - V_{FF}^2(E - \mathcal{E}_W) \quad (25)$$

and Green's functions:

$$\begin{aligned}G_{00} &= \frac{(E - \mathcal{E}_F - \frac{V_{FF}^2}{E - \mathcal{E}_F})(E - \mathcal{E}_F) - V_{WF}V_{FW}}{\Theta} \\ G_{01} &= \frac{V_{WF}(E - \mathcal{E}_F)}{\Theta} \\ G_{02} &= \frac{V_{WF}V_{FF}}{\Theta} \\ G_{12} &= \frac{(E - \mathcal{E}_W)V_{FF}}{\Theta}\end{aligned}\quad (26)$$



and for the system with 3 generations of dendrimeric chains (Fig.5d):

$$\Theta = (E - \mathcal{E}_W) \frac{1}{G_1 G_2 G_3} + V_{WF} V_{FF}^3 - \frac{V_{WF}^2}{G_2 G_1} - \frac{V_{FF}^2 (E - \mathcal{E}_W)}{G_3} - \frac{(E - \mathcal{E}_W) V_{FF}^2}{G_1} \quad (27)$$

with the loop values:

$$\begin{aligned} \frac{1}{G_3} &= E - \mathcal{E}_F \\ \frac{1}{G_2} &= E - \mathcal{E}_F - \frac{V_{FF}^2}{E - \mathcal{E}_F} \\ \frac{1}{G_1} &= E - \mathcal{E}_F - 2 \frac{V_{FF}^2}{E - \mathcal{E}_F} \end{aligned} \quad (28)$$

And similarly to (26) we also calculated the Green's function matrix elements  $G_{01}, G_{12} \dots G_{33}$ .

In this way we always can calculate Green's function matrix for the cases of more generations.

Note here that the energy of the new excitation in the system, i.e. the energy of the Wannier-Frenkel hybrid exciton is the zero condition for  $\Theta$  (25), (27). The energy and also the Green functions depend on the energies of both the Wannier and the Frenkel excitons, on the effective interactions coefficient, and the structure of the dendrimer branches. So the geometry of the dendrimer, the number of the branches are very important. To change the geometry of the quantum dot- dendrimer system, we will change the energy of the hybrid exciton and then the optical processes of the system.

## VI. The quantum dot-dendron ligand

In recent time several series of semiconductor nanocrystal- organic dendron ligands, an objective which has hyperbranched organic molecules, have been designed and synthesized [5]. The priority of the dendron ligand is perfect symmetry with the dot at the center, and also the closely packed ligand shell.

We can apply the diagram method to study the hybrid excitation for this model dendron. We will consider in this section the ligand model we mentioned in section II. A quantum dot is attached with three branches, then each terminal molecule is attached to other two branches, and so on (Fig.1). At first we consider the first generation system with the quantum dot at the center attached to 3 chains of molecule (Fig. 6a). Consider this system like a linear chain of the chain 1, the dot and the chain 3. the chain 2 then is considered as the chain 2' attaching to the dot. For this case we have:

$$\begin{aligned} G_{11} &= \frac{1}{\Theta} [(E - \tilde{\mathcal{E}}_2)(E - \mathcal{E}_3) - V_{12} V_{21}] \\ G_{12} &= \frac{1}{\Theta} V_{12} (E - \mathcal{E}_3) = G_{21} \\ G_{13} &= \frac{1}{\Theta} V_{12} V_{23} = G_{31} \\ G_{22} &= \frac{1}{\Theta} (E - \mathcal{E}_1)(E - \mathcal{E}_3) \end{aligned}$$

$$\begin{aligned}
G_{23} &= \frac{1}{\Theta}(E - \mathcal{E}_1)V_{23} = G_{32} \\
G_{33} &= \frac{1}{\Theta}[(E - \mathcal{E}_1)(E - \tilde{\mathcal{E}}_2) - V_{23}V_{32}]
\end{aligned} \tag{29}$$

and

$$\Theta = (E - \mathcal{E}_1)(E - \tilde{\mathcal{E}}_2)(E - \mathcal{E}_3) - V_{12}V_{21}(E - \mathcal{E}_3) - V_{23}V_{32}(E - \mathcal{E}_1) \tag{30}$$

where the value of the loop at site 2 (the dot) is including the side graph

$$\tilde{\mathcal{E}}_2 = \mathcal{E}_2 - \frac{V_{22'}V_{2'2}}{E - \mathcal{E}_{2'}} \tag{31}$$

In the language of Wannier and Frenkel exciton, then we have for the Green functions of the system:

$$\begin{aligned}
G_{11} &= \frac{1}{\Theta}[(E - \mathcal{E}_W - \frac{V_{WF}V_{FW}}{E - \mathcal{E}_F})(E - \mathcal{E}_F) - V_{FW}V_{WF}] \\
G_{12} &= \frac{1}{\Theta}V_{FW}(E - \mathcal{E}_F) = G_{21} \\
G_{13} &= \frac{1}{\Theta}V_{FW}V_{WF} = G_{31} \\
G_{22} &= \frac{1}{\Theta}(E - \mathcal{E}_F)^2 \\
G_{23} &= \frac{1}{\Theta}(E - \mathcal{E}_F)V_{WF} = G_{32} \\
G_{33} &= \frac{1}{\Theta}[(E - \mathcal{E}_F)(E - \mathcal{E}_W - \frac{V_{WF}V_{FW}}{E - \mathcal{E}_F}) - V_{FW}V_{WF}]
\end{aligned} \tag{32}$$

and

$$\Theta = (E - \mathcal{E}_F)^2(E - \mathcal{E}_W - \frac{V_{WF}V_{FW}}{E - \mathcal{E}_F}) - V_{FW}V_{WF}(E - \mathcal{E}_F) - V_{WF}V_{FW}(E - \mathcal{E}_F) \tag{33}$$

For the two generation quantum dot-dendron, we can consider the dendron as linear chain of one generation with sidegroup attached to each of the terminal molecules (Fig.6b). Then the loop value  $\mathcal{E}_1, \mathcal{E}_2, \mathcal{E}_3$  become

$$\begin{aligned}
\tilde{\mathcal{E}}_1 &= \mathcal{E}_1 - \frac{V_{1,11}V_{11,1}}{E - \mathcal{E}_{11}} - \frac{V_{1,12}V_{12,1}}{E - \mathcal{E}_{12}} \\
\tilde{\mathcal{E}}_3 &= \mathcal{E}_3 - \frac{V_{3,31}V_{31,3}}{E - \mathcal{E}_{31}} - \frac{V_{3,32}V_{32,3}}{E - \mathcal{E}_{32}} \\
\tilde{\mathcal{E}}_1' &= \mathcal{E}_1' - \frac{V_{2',2'1}V_{2'1,2'}}{E - \mathcal{E}_{2'1}} - \frac{V_{2,2'2}V_{2'2,2'}}{E - \mathcal{E}_{2'2}}
\end{aligned} \tag{34}$$

Replace these values into the formulae for the Green function (29), we have Green's functions for hybrid exciton in the system of 2 generation of dendrimer.

Continue this process of sidegroup graph attached to those three chains of the first generation, practically we can go farther to any generation just by changing the loop values

in (29). Since every branching point is attached to two branches, in going from  $n$  generation to  $n+1$  generation, the value of the loop  $i$  just needs addition by the value of the two branches of  $n+1$  generation attached to the generation  $n$  of the loop:

$$\mathcal{E}_i^{\tilde{n}+1} = \mathcal{E}_i^{\tilde{n}} - \frac{V_{in;in+1,1}V_{in+1,1;in}}{E - \mathcal{E}_{i,n+1,1}} - \frac{V_{in;in+1,2}V_{in+1,2;in}}{E - \mathcal{E}_{i,n+1,2}} \quad (35)$$

where 1 and 2 denote the two branches of the  $n+1$  generation. From here, if we know the energy and Green's function of the dendrimer with  $n$  generations, we always can go to the dendrimer with  $n+1$  generations. Because of the continuous fraction, from some generation, the effects of  $n+1$  generation is small and can be treated as some small perturbations.

The energy of the Wannier-Frenkel hybrid exciton again is the pole of the Green functions, or in another words, is obtained from the condition for the zeros of the Green's function determinator  $\Theta$ . For example for the quantum dot-dendron ligand of one generation the equation (33) gives us:

$$E^{W-F} = \frac{1}{2}[\mathcal{E}_F + \mathcal{E}_W \pm \sqrt{(\mathcal{E}_F - \mathcal{E}_W)^2 + 8V_{WF}V_{FW}}] \quad (36)$$

and for the quantum dot-dendron ligand of two generation we have for energy of the hybrid exciton:

$$E^{W_F} = \frac{1}{2}(\mathcal{E}_F + \mathcal{E}_W + \frac{4V_{FF}^2}{E - \mathcal{E}_F} - \frac{2V_{WF}^2}{E - \mathcal{E}_W} \pm [\mathcal{E}_F^2 + \mathcal{E}_W^2 + 6\mathcal{E}_W\mathcal{E}_F + \frac{16V_{WF}^4}{(E - \mathcal{E}_F)^2} - \frac{16V_{FF}^4}{(E - \mathcal{E}_F)^2} + \frac{24V_{FF}^2V_{WF}^2}{(E - \mathcal{E}_F)^2} + 8V_{WF}^2]^{1/2}) \quad (37)$$

we mention here that using the continuous fractional diagram technique, each time when we have more generations, the values of  $\frac{2V_{FF}^2}{E - \mathcal{E}_F}$  are added to each branching point. It means when one more generation is added, in the equation (33) only the value of  $E$  will change for  $\frac{2V_{FF}^2}{E - \mathcal{E}_F}$  time some integers. Then for  $n$  large when it is difficult to solve (33) analitically, the self-consistent method is used to solve the equation, so for quantum dot-dendrom ligands of any generation we always have expressions for the energy of the hybrid exciton.

For a simply illustrative numerical calculation we use CdSe quantum dot with pentacene dendrimer. If the radius of the dot is 3.8 nm  $E^W = 2.1ev$ ,  $E^F = 1.5ev$ ,  $\mu^F = 5D$ ,  $\mu^W = 10D$ . Assume there are 4 molecules in one chain then there are two values of hybrid exciton  $E^{W_F} = 2.1035ev$  and  $E^{W_F} = 1.4996ev$ . It means there are two hybrid exciton values close to the Wannier and Frenkel excitons, with a shift of about 0.4 meV. If we use tetracene dendrimer with Frenkel exciton energy  $E^F = 2ev$ , closer to energy of the Wannier exciton in the quantum dot, then we get two values for the hybrid exciton at  $E^{W_F} = 2.1019ev$  and  $E^{W_F} = 1.9981ev$ , or the shift is about 1.95 meV. So if we choose the size of dot and material of dendrimer so that the energies of the Wannier and Frenkel excitons are close, the effect of hybridization is larger. The structure of the dendrimer (number of molecule in one branch, for instance), also decides the hybridization.

Green's functions are quantities to characterize a many-particle system, so obtaining Green's functions gives a lot of information of the system. Since any particular observable can be calculated using the Green's function relations such as

$$\langle O \rangle = i \int dx dx' O(xx') G(xt|x't+) \quad (38)$$

we can use the real-time components of the Green's functions (29) to calculate physical quantities of the systems.

### **Summary**

In this paper we propose a model to study the organic-semiconductor hybrid exciton in quantum dot-dendrimer system. The energy of the hybrid exciton as well as the Green's function matrix elements for different quantum dot-dendrimer systems have been calculated. With the Green's functions the optical properties and optical processes are expected to be obtained. By changing structure and parameter of the systems, the optical properties can be controlled as interested. The use of these Green Functions to calculate optical and other response functions will be discussed elsewhere (see Ref. 17).

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## FIGURE CAPTIONS

**Fig.1.** A Quantum Dot- Dendron Ligand Model .

**Fig.2** a) A quantum dot-molecule chain. b) A molecule-molecule chain.

**Fig.3.** a)Linear chain of localized sites. b)Linear chain with three vertices. c)Cyclic value of the graph for linear chain of three vertices

**Fig.4.** a) A chain with a side group attached to the site  $i$ . b)A graph of a side group.

**Fig. 5** a)A quantum dot-dendrimer slice. b) A QD-dendrimer slice as a side group graph. c) A slice of two generations. d)A slice of three generations.

**Fig.6.** a)A QD- dendron ligand with one generation. b)A QD- dendron ligand with two or more generations.

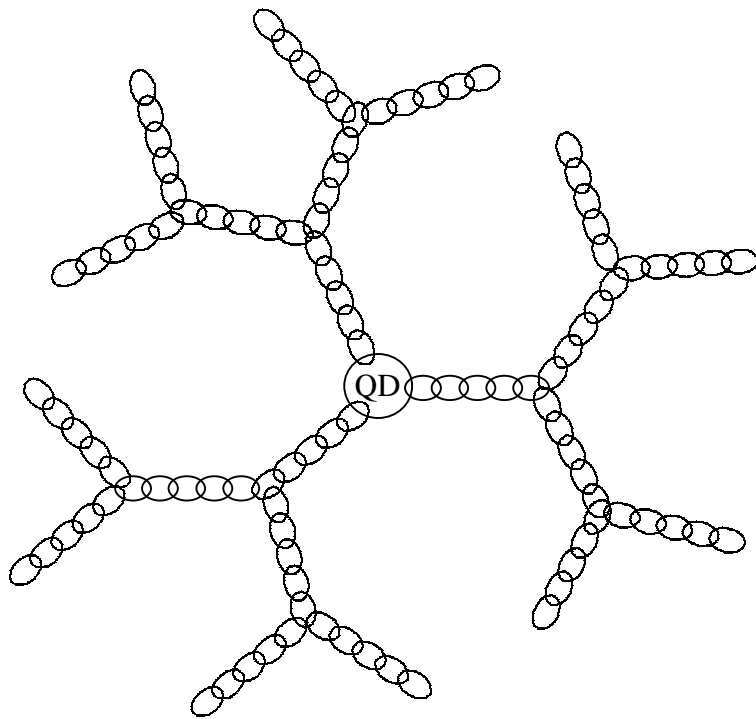


Fig. 1

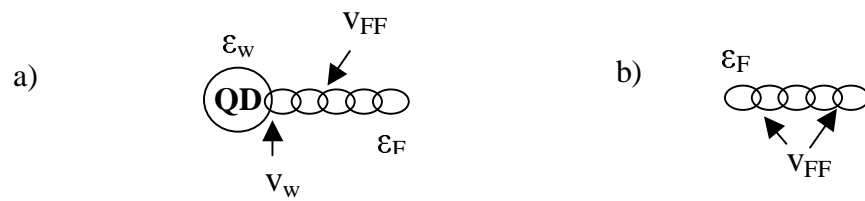
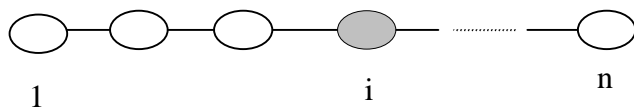


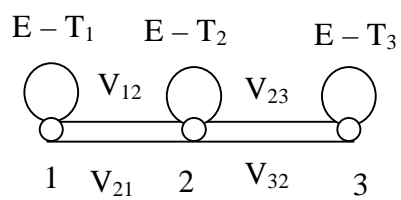
Fig. 2



a)



b)



c)

$$\begin{aligned}
 \theta(\Gamma) = & \begin{array}{c} E - T_1 \\ \text{loop} \\ \textcircled{1} \end{array} \times \begin{array}{c} E - T_2 \\ \text{loop} \\ \textcircled{2} \end{array} \times \begin{array}{c} E - T_3 \\ \text{loop} \\ \textcircled{3} \end{array} \\
 & + \begin{array}{c} V_{12} \\ \text{---} \textcircled{1} \text{---} \textcircled{2} \text{---} \\ V_{21} \end{array} \times \begin{array}{c} E - T_3 \\ \text{loop} \\ \textcircled{3} \end{array} \\
 & + \begin{array}{c} E - T_1 \\ \text{loop} \\ \textcircled{1} \end{array} \times \begin{array}{c} V_{23} \\ \text{---} \textcircled{2} \text{---} \textcircled{3} \text{---} \\ V_{32} \end{array}
 \end{aligned}$$

Fig. 3

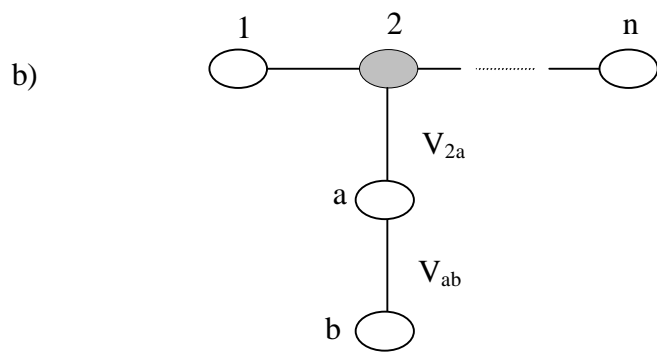
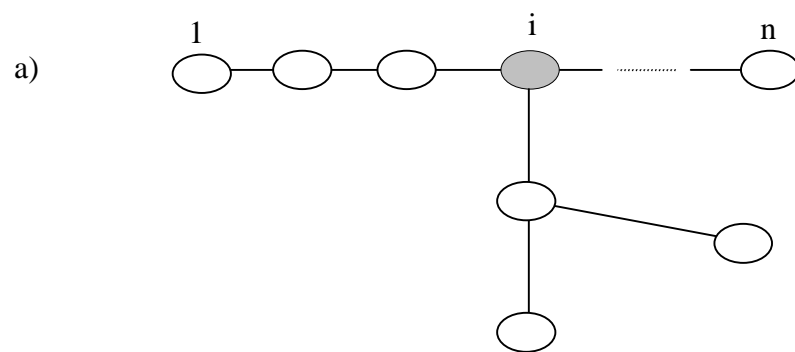


Fig. 4

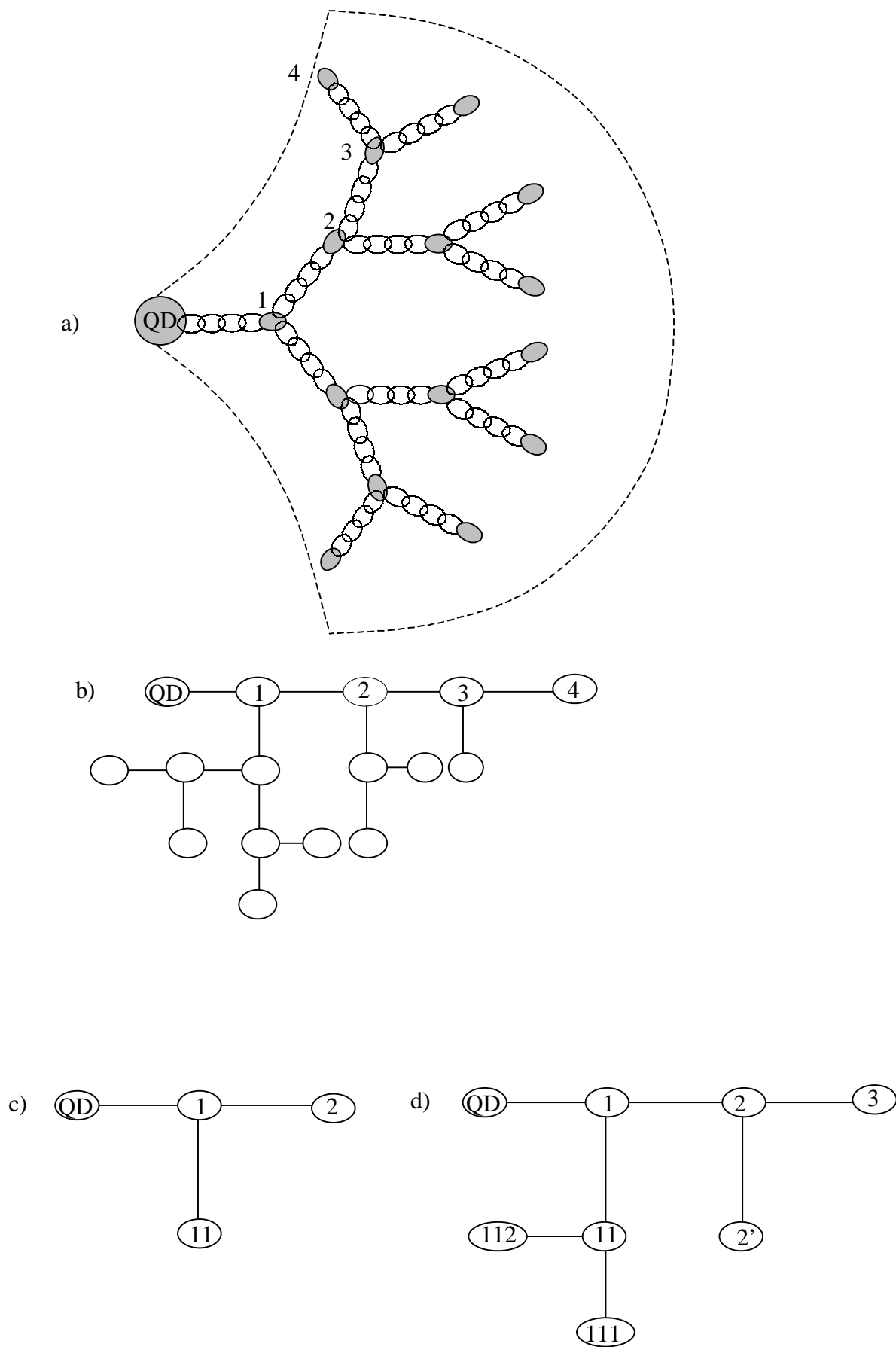


Fig. 5

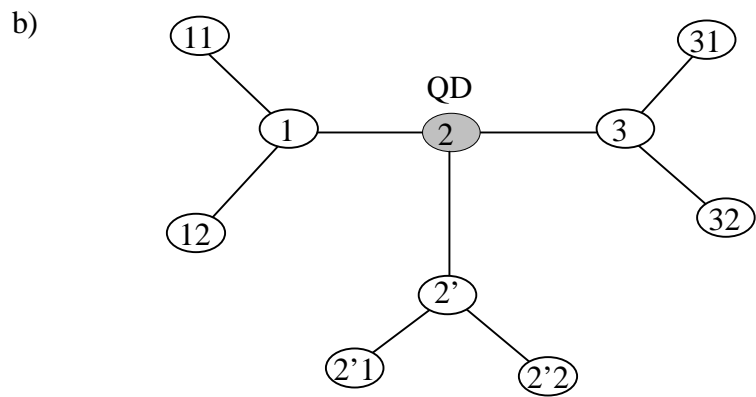
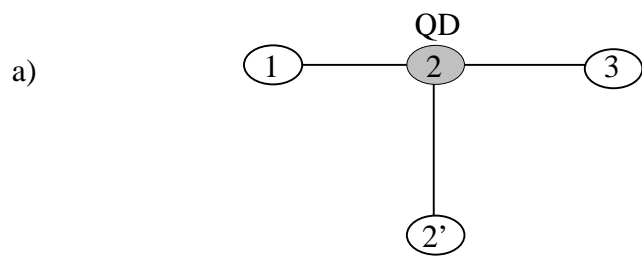


Fig. 6